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Theoretical and Experimental Investigation
of Nonlinear Optoacoustics in Liquids

Stanley A. Cheyne and Henry E. Bass

Physical Acoustics Research Laboratory
University of Mississippi
University, Mississippi 38677
PARGUM 89-01

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ABSTRACT

THEORETICAL AND EXPERIMENTAL INVESTIGATION OF NONLINEAR OPTOACOUSTICS IN LIQUIDS

CHEYNE, STANLEY ALAN. B.A., Hendrix College, 1984. M.A., University of Mississippi, 1986. Ph.D., University of Mississippi, 1989. Dissertation directed by Frederick A. P. Barnard Distinguished Professor Henry E. Bass.

The optoacoustic effect in liquids has been studied theoretically and experimentally. Measurements were taken in various liquids studying the thermal expansion mechanism and comparing these results to existing theoretical predictions. Among the quantities investigated were the dependence of optoacoustic amplitude on optical absorption coefficient, thermal expansion coefficient and laser pulse energy. These experimental observations were found to be in agreement with theory. The signal amplitude was also measured as a function of propagation distance. It was found that the optoacoustic amplitude varies as $1/\sqrt{r}$ which is characteristic of a cylindrical source. Measurements were also taken in liquid Carbon Disulfide (CS_2). The strong absorption of the 337 nm radiation resulted in a nonlinear relationship between optoacoustic amplitude and input energy. These nonlinear variations were explained in terms of dynamically changing temperature dependent coefficients of thermal expansion and optical absorption.



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Chapter I

Introduction

In 1881, Alexander Graham Bell discovered that the periodic interruption of focused sunlight on a dark substance produced audible sound.¹ As the substance absorbed the sunlight, its temperature began to rise. The substance cooled as the absorbed energy was dissipated. Expansion of the air near the surface of the substance occurred with the temperature increase while contraction occurred with the cooling process. These rapid expansions and contractions of the air caused density variations which resulted in pressure changes. These pressure variations were the source of audible sound detected by Bell.

Bell had high expectations for possible applications of his discovery. He envisioned using sunlight for communication systems between cities; however, the idea of having a system of lenses carrying sunlight from city to city seemed improbable. His insight as applied to "optoacoustic" spectroscopy in gases however, has become a reality.

With the invention of the laser in the early 1960's came renewed interest in optically induced sound, or optoacoustics.^{2,3} Laser light has desirable characteristics which are advantageous in

optoacoustic generation. One feature is that it is coherent radiation which can be tightly focused to create high energy densities. This allows good control of the amplitude and frequency of the acoustic wave generated. Another feature is that laser light is monochromatic in nature. Having control of the optical wavelength of operation allows one to be very selective and precise in determining which internal state the optical source excites.

Optoacoustic investigations have been carried out and applied in a variety of different research areas. An intensive effort in determining and understanding the underlying physical processes involved has been occurring since the early 1960's.⁴⁻¹⁰ Absorption spectroscopy, fluorescence lifetime, and other internal energy transfer studies are only a few of the applied areas of research.¹¹⁻²² In addition to these microscopic investigations, optoacoustic techniques are used to determine macroscopic properties of substances, or material characterization.^{23,24} Other studies involved the effects of a moving source as a means of increasing the optoacoustic conversion efficiency.²⁵⁻²⁹

The known mechanisms for optoacoustic generation in order of increasing efficiency are electrostriction, thermal expansion, vaporization, and dielectric breakdown. Electrostriction occurs when a region of higher relative electric permittivity moves into a region of lower relative electric permittivity and higher electric field. The electric permittivity is proportional to the square of the index of refraction which in turn is proportional to the density of the fluid.

The density immediately outside the excitation zone is suddenly increased upon absorption of a laser pulse due to the outward going compressional wave. The region outside the excitation zone moves toward the source region where the relative electric permittivity is now lower and the electric field is higher due to the laser pulse. As a result, a rarefactional acoustic wave is generated. The familiar thermal expansion mechanism involves rapid heating and cooling of a liquid which, in turn, causes expansions and contractions resulting in density and pressure changes in the medium. These pressure variations produced within the medium are the origin of the acoustic responses. At higher energy densities, it is possible to vaporize a liquid. The coefficient of thermal expansion of a gas is larger than that of a liquid. Since the amplitude of the optoacoustic wave is directly proportional to the thermal expansion coefficient, the optoacoustic conversion efficiency should increase after the vaporization threshold is achieved. Dielectric breakdown occurs when the electric field within a liquid or around an impurity reaches such a high value that an electric discharge occurs. Associated with this discharge is local ionization, local heating, and probably cavitation, all of which contribute to the acoustic wave.

The medium subjected to the optical source is important in determining the magnitude of the acoustical output. Bell found that it was easier to produce sound in gases than in liquids. Although liquids typically absorb more light, gases have lower densities allowing them to expand more for a given temperature change. For

this reason, early spectroscopic optoacoustic studies were done mostly in gases. Energy transfer studies were first done in gases mainly because reaction rates were relatively slow. Also, the equilibrium pressure of gases can be altered to change the rate of molecular collisions, and hence the reaction rates. Relaxation times in liquids are much faster than those present in gases since multibody interactions between molecules are more likely.³⁰ Collision rates cannot be controlled by changing equilibrium pressure since liquids are essentially incompressible; hence, investigations in liquids must be capable of resolving events on a much shorter time scale than those done in gases.

The purpose of this study is to provide a microscopic and macroscopic description of the optoacoustic effect in liquids. In addition, we wish to explore the vaporization process more closely in hopes of gaining more knowledge on the nature of liquids. We also plan to investigate the dependence of pressure amplitude on laser pulse energy.

Chapter II explains the thermal expansion mechanism from a microscopic and macroscopic viewpoint. This is the basis for the linear theory of optoacoustics. Chapter II also discusses how the nonlinear effects evolve from the linear theory which is manifested macroscopically as vaporization. Chapter II also gives a mathematical derivation of the acoustic pressure including effects due to strong and weak optical absorption and internal relaxation processes occurring in the liquid.

Chapter III gives a description of the experimental apparatus involved. It explains how the penetration depth of a strongly absorbing fluid is determined. Chapter III also describes how the dimensions of the UV laser beam at the focal point are determined.

Chapter IV compares linear and nonlinear experimental observations with theory.

Chapter V gives a summary of conclusions and recommendations for future work.

Chapter II

Theory

A. Microscopic Interpretation

A microscopic description of optoacoustics in liquids must consider the nature of the recipient molecules and the wavelength of the incoming photons. In general, the optical energy is first absorbed by molecules in the fluid resulting in excitation of electronic, vibrational, and/or rotational states depending on the wavelength of the photon. For example, IR and microwave radiation excite vibrational and rotational states of the molecules respectively. The excess internal energy then transfers to translation through the most probable energy transfer pathway. At the UV wavelengths employed in this experiment, the laser photons excite an electronic state of the molecules. Part of the electronic energy is converted to vibrational and translational energy which is manifested macroscopically as thermal expansion of the fluid. Typically, deexcitation via fluorescence also occurs when an electronic state is excited, however, this is not always the case.

Gournay³¹ and Hsieh³² have shown that the optoacoustic conversion efficiency does not depend on the optical wavelength of

excitation but on the total pulse energy of deposition. IR lasers produce photons with insufficient energy to cause electronic excitation, yet the efficiency at which the electromagnetic energy is converted to thermal expansion is identical to that for UV lasers (at least in the linear regime). Since the observed thermal expansion depends only upon the total energy deposited in the fluid and not on the optical wavelength, we conclude that it is vibrational and/or translational modes which give rise to expansion.

Thompson *et al.*²² found that following deposition of energy in CS₂ by a UV laser, there was a time lag for resultant thermal expansion of about 90 ns which is associated with vibrational relaxation of the ν_3 asymmetric stretch mode of CS₂ to translation as well as a time constant of 1.5 ns for vibrational relaxation of the ν_2 bending mode of CS₂. These results indicate that when energy is added to the fluid, it must undergo internal conversion processes which occur on a nanosecond time scale prior to causing thermal expansion. Since the laser used has a pulse length of 800 ps, essentially all the laser energy deposited resides in internal states at the end of the pulse. This result along with the large optical absorption coefficient of CS₂ reveals interesting nonlinear phenomena which will be discussed in more detail later.

To fully understand the physical processes taking place as the laser light interacts with the fluid, one must also examine the molecular structure of liquids. The liquid state has been an intriguing problem to physicists and chemists alike due to its

complexity and constantly changing nature. Historically, there are several ways to view a liquid.³³

The first is to envision the liquid as a dense gas. This involves mathematically compressing a gas down to liquid densities and allowing existing theories to run their course. This approach has proven successful in predicting only a few properties of liquids. Van der Waals modified the ideal gas law taking in consideration the molecular interactions. He arrived at the well known result

$$(P+a/V^2)(V-b)=RT.$$

The constant a accounts for the long range attractive forces between molecules while b is associated with the short range repulsive forces due to the finite volume of their molecules.³⁴ This model is successful in predicting the behavior of a few substances at liquid-gas interfaces.

A second way to view a liquid is as an imperfect solid. This model is the basis of the so-called lattice theory of liquid structure. Molecules at particular lattice sites are allowed to vibrate or wander about interacting with neighboring molecules possibly even filling a hole. A hole is simply a lattice site vacant of a molecule.

A third way to model a liquid is with the use of distribution functions. The radial distribution function $g(r)$ is the probability of finding two molecules a distance r apart. By the use of X-ray diffraction experiments, $g(r)$ can be obtained. Examinations of these

results reveal that liquids have short range structure similar to solids and long range structure similar to gases. Theoretical expressions for $g(r)$ involve knowledge of intermolecular forces between the molecules of the system. Mansoori and Haile³⁵ define the molecular distribution function as "the probability of finding sets of molecules in particular statistical mechanical configurations."

A microscopic description of optoacoustics must consider the interactions taking place between photons and molecules. The most physically appealing model to explain optoacoustic phenomena is to envision the liquid as being composed of molecular groups, clusters.³⁶ The most probable number of molecules in a cluster varies depending on the liquid. The cluster size also depends on the temperature of the fluid. Clusters are larger at lower temperatures. As the temperature increases, the cluster size decreases. Consider a cluster of size N_{T_0} where N_{T_0} equals the number of molecules in the cluster at room temperature T_0 . A photon of energy E_γ is absorbed by the cluster causing molecules to vibrate, reorient, or be removed from the group entirely. Molecules removed from the cluster will recombine with its host or a neighboring cluster in a time corresponding to some recombination time τ_r .

Suppose that the cluster is subjected to an additional photon in a time less than τ_r , that is, before the perturbed molecules have a chance to recombine. There is then some probability of removing an additional molecule from the cluster, hence decreasing the localized density further. As the number of photons per unit time increases,

the probability of removing more molecules from their associated cluster continues to increase. The density continues to decrease eventually attaining values corresponding to the gas phase, hence forming a vapor bubble in the region of highest photon density. It takes a certain amount of energy E_n to remove n molecules from their cluster. If E_γ equals E_n , then n molecules will be removed. If the cluster absorbs two photons of energy E_γ , then it is possible that more than n molecules will be removed. In other words, it is not necessary that only one photon removes only one molecule. In the high energy limit, all molecules should be free from clusters resulting in an ideal gas.

B. Macroscopic Interpretation

The theoretical treatment of optoacoustics by the thermal expansion mechanism has been carried out by several authors.⁴⁻⁹ Others have included electrostriction contributions as well.^{37,38} Hutchins and Tam have shown that electrostriction is negligibly small compared to thermal expansion and can be ignored unless optical absorption is very small.²⁴ We have adopted the theory developed by Lai and Young neglecting any contributions from electrostriction.³⁷ We begin by writing down the equation of motion

$$\rho \frac{\partial^2 \mathbf{x}(r,t)}{\partial t^2} = - \nabla p(r,t) \quad (2.1)$$

where ρ is the density, $\mathbf{x}(r,t)$ is the acoustic displacement, and p is

the acoustic pressure. The expansion equation can be written as

$$\nabla \cdot \mathbf{x}(r,t) = -\frac{p(r,t)}{\rho c^2} + \beta T \quad (2.2)$$

where T is the temperature increase c is the speed of sound in the liquid, and β is the coefficient of thermal expansion. Taking a second time derivative of Eq. 2.2 and substituting into Eq. 2.1

$$-\frac{1}{\rho} (\nabla \cdot \nabla p(r,t)) = -\frac{1}{\rho c^2} \frac{\partial^2 p(r,t)}{\partial t^2} + \beta \frac{\partial^2 T}{\partial t^2} \quad (2.3)$$

or

$$\left(\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2 \right) p(r,t) = \rho \beta \frac{\partial^2 T}{\partial t^2}. \quad (2.4)$$

From setting h , the specific enthalpy, equal to the laser pulse energy E divided by the mass of the liquid, we find

$$c_p = \frac{1}{\rho V} \left(\frac{dE}{dT} \right) \quad (2.5)$$

or

$$dT = \frac{1}{\rho V c_p} dE \quad (2.6)$$

where V is equal to the cross sectional area A of the laser beam divided by the optical absorption coefficient α of the liquid. Taking the time derivative of Eq. 2.6

$$\frac{\partial T}{\partial t} = \frac{\alpha}{\rho c_p A} \frac{\partial E}{\partial t} \quad (2.7)$$

The intensity I of the laser beam is the energy per unit time per unit area so

$$\frac{\partial T}{\partial t} = \frac{\alpha}{\rho c_p} I, \quad (2.8)$$

and

$$\frac{\partial^2 T}{\partial t^2} = \frac{\alpha}{\rho c_p} \frac{\partial I(r,t)}{\partial t} \quad (2.9)$$

Substituting Eq. 2.9 into Eq. 2.4

$$\left(\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2\right)p(r,t) = \frac{\alpha\beta}{c_p} \frac{\partial I(r,t)}{\partial t} . \quad (2.10)$$

If we let

$$\left(\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2\right)\phi(r,t) = I(r,t) \quad (2.11)$$

where $\phi(r,t)$ is a velocity potential, then Eq. 2.10 becomes

$$p(r,t) = \frac{\alpha\beta}{c_p} \frac{\partial \phi(r,t)}{\partial t} . \quad (2.12)$$

If we use a Gaussian intensity distribution described by Lai and Young as

$$I(r,t) = \frac{E}{2\pi^{3/2}} \frac{1}{R^2 \tau_p} \exp\left(-\frac{r^2}{2R^2} - \frac{t^2}{2\tau_p^2}\right) , \quad (2.13)$$

then Eq. 2.10 has a solution

$$\phi(r,t) = \frac{E}{\pi\sqrt{8}} \left(\frac{c}{r}\right)^{1/2} \frac{1}{\tau_e^{1/2}} \Phi_0\left(\frac{t'}{\tau_e}\right) \quad (2.14)$$

where

E = laser pulse energy,

c = acoustic velocity,

r = propagation distance,

$\tau_e = (\tau_p^2 + \tau_a^2)^{1/2}$,

τ_p = time duration of laser pulse,

τ_a = acoustic transit time,

t' = retarded time,

R = excitation beam radius, and

$$\Phi_0(\xi) = \sqrt{\frac{\pi}{8}} |\xi|^{1/2} \left[\frac{\sqrt{2}}{\pi} K_{1/4}\left(\frac{\xi^2}{4}\right) + 2\Theta(\xi) I_{1/4}\left(\frac{\xi^2}{4}\right) \right] \exp\left(-\frac{\xi^2}{4}\right).$$

Here,

$$\xi = \left(t - \frac{r}{c}\right) / \tau_e,$$

Θ = Heaviside step function, and

$K_{1/4}$ and $I_{1/4}$ are imaginary Bessel functions of 1/4 order.⁴⁵ The time evolution of the optoacoustic wave is described by Φ_0 where the pressure amplitude A is given by the remaining portion of Eq. 2.14 and Eq. 2.12 as

$$A = \frac{\alpha\beta}{c_p} \frac{E}{\pi\sqrt{8}} \left(\frac{c}{r}\right)^{1/2} \tau_e^{-1/2}. \quad (2.15)$$

C Theoretical Treatment for Large Optical Absorption and Internal Relaxation

The theoretical treatment of CS₂ is approached using a different method. In the case of CS₂, optical absorption is very strong. Thompson *et al.*²² have shown that slow internal relaxation in CS₂ also affects the optoacoustic wave. As a result, the differential equation is solved with a Green's function technique. The spatial profile of the laser pulse is modelled as a Gaussian distribution. Relaxation and absorption are also included by describing the intensity distribution as

$$I(r,t) = \left(\frac{A_1}{\tau_1} e^{-t/\tau_1} + \frac{A_2}{\tau_2} e^{-t/\tau_2}\right) e^{-\rho^2/a^2 - \alpha z} \quad (2.16)$$

where a is the excitation beam radius, α is the optical absorption coefficient, ρ is the radial distance from the beam axis, z is the distance down the beam axis, and A_1, A_2, τ_1, τ_2 are found from the relaxation equation. The quantities τ_1 and τ_2 represent relaxation times of internal states in a molecule. The quantities A_1 and A_2 are the relative strengths of the corresponding relaxation times. The solution to Eq. 2.11 using a Green's function approach is

$$\phi(\mathbf{r}, t) = \frac{1}{4\pi} \int_v \frac{dV_0}{R} I(\mathbf{r}_0, t-R/c) \quad (2.17)$$

where $|\mathbf{r}_0| = (\rho_0^2 + z_0^2)^{1/2}$ is the source point, $R = |\mathbf{r} - \mathbf{r}_0|$, and dV_0 is an infinitesimal volume element of integration. Substituting Eq. 2.16 into Eq. 2.17 and separating time and space dependence,

$$\phi(\mathbf{r}, t) = \frac{1}{4\pi} \int_v \frac{dV_0}{R} g(\mathbf{r}_0) f(t-R/c) \quad (2.18)$$

where

$$g(\mathbf{r}_0) = \exp(-\rho_0^2/a^2 - \alpha z_0) \quad (2.19)$$

and

$$\begin{aligned} f(t) &= \frac{A_1}{\tau_1} e^{-t/\tau_1} + \frac{A_2}{\tau_2} e^{-t/\tau_2} ; t \geq 0 \\ &= 0 ; t < 0. \end{aligned} \quad (2.20)$$

The acoustic pressure can be found by numerically integrating Eq. 2.18 and then taking the time derivative; however, it is more efficient in the numerical calculation to define a time dependent delta function response

$$u(\mathbf{r},t) = \frac{1}{4\pi} \int_v \frac{dV_0}{R} g(\mathbf{r}_0) \delta(t-R/c) \quad (2.21)$$

and convolve it with $f(t)$ to obtain

$$\phi(\mathbf{r},t) = u(\mathbf{r},t) * f(t) \quad (2.22)$$

or

$$\phi(\mathbf{r},t) = \int_0^t u(\mathbf{r},t-t')f(t')dt' . \quad (2.23)$$

The acoustic pressure is found by evaluating Eq. 2.12 replacing $\phi(\mathbf{r},t)$ with Eq. 2.23

$$p(\mathbf{r},t) = \frac{\alpha\beta}{c_p} \frac{d}{dt} \int_0^t u(\mathbf{r},t-t')f(t')dt' . \quad (2.24)$$

Using Leibnitz's rule and noting $u(\mathbf{r}, 0) = 0$, Eq. 2.24 can be written as

$$p(\mathbf{r},t) = \frac{\alpha\beta}{c_p} \int_0^t \frac{\partial}{\partial t} [u(\mathbf{r},t-t')f(t')] dt' . \quad (2.25)$$

Substituting Eq. 2.21 into Eq. 2.25

$$p(\mathbf{r},t) = \frac{\alpha\beta}{c_p} \frac{1}{4\pi} \int \frac{dV_0}{R} g(\mathbf{r}_0) \int_0^t \frac{\partial}{\partial t'} [\delta(t-t'-R/c)] f(t') dt'. \quad (2.26)$$

Since

$$\frac{\partial}{\partial t} \delta(t-t'-R/c) = - \frac{\partial}{\partial t'} \delta(t-t'-R/c), \quad (2.27)$$

Eq. 2.26 becomes

$$p(\mathbf{r},t) = - \frac{\alpha\beta}{c_p} \frac{1}{4\pi} \int \frac{dV_0}{R} g(\mathbf{r}_0) \int_0^t \frac{\partial}{\partial t'} [\delta(t-t'-R/c) dt'] f(t') dt'. \quad (2.28)$$

Integrating Eq. 2.28 by parts yields the acoustic pressure

$$p(\mathbf{r},t) = \frac{\alpha\beta}{c_p} \int_0^t \frac{\partial f(t')}{\partial t'} u(\mathbf{r},t-t') dt' + u(\mathbf{r},t) f(0). \quad (2.29)$$

Comparison of Eq. 2.29 to experimental measurements in Carbon Disulfide and Propanol can be found in Ref. 22.

Chapter III

Experimental Work

A. Experimental Configuration

The experimental configuration is patterned after Sullivan and Tam.³⁹ The principal components consist of two lasers. A pulsed laser is used as a source and a continuous wave(cw) laser is used to detect the optoacoustic signal. The experimental system is shown in Figure 3.1.

A model number LN 1000 nitrogen laser manufactured by Photochemical Research Associated Inc. (PRA) was used as the excitation source. It is an atmospheric pressure laser which emits ultraviolet (UV) pulses at a wavelength of 337 nm. The maximum energy per pulse is 1 mJ. The pulse duration is 800 ps (manufacturer specification) giving a maximum peak power of 1.25 MW.

The UV pulse first encounters a right angle prism where a small percentage of the beam is reflected to the trigger photodiode. This photodiode was an Oriel Corporation model number 7185 with a rise time of about 9 ns. The major portion of the beam passes unperturbed to a collimating lens. This is a fused silica lens having a diameter of 2.54 cm and a focal length of 100 cm. The pulse is then

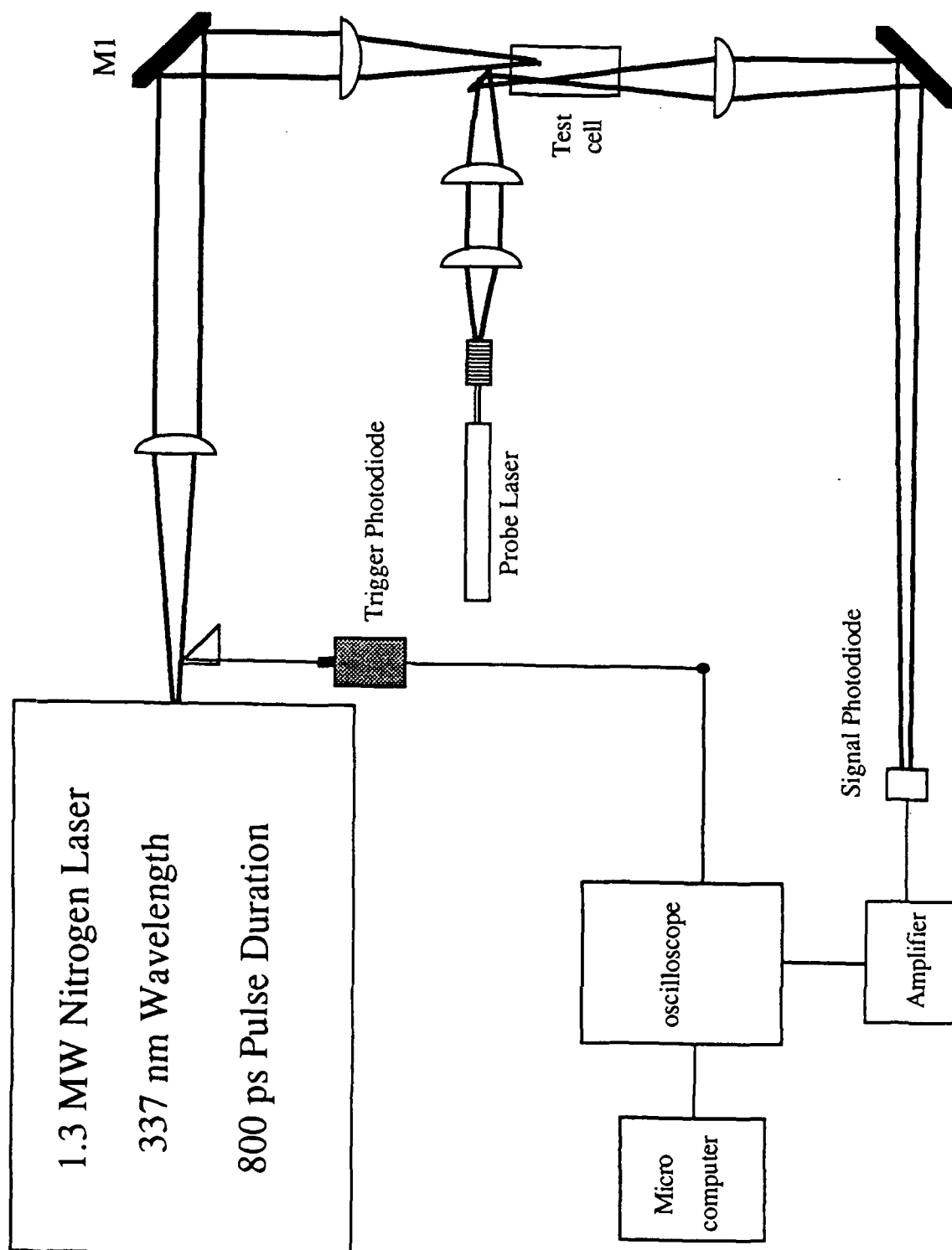


Figure 3.1

reflected ninety degrees by a 5.08 cm silver-coated front-surfaced mirror. It then impinges on a quartz fluorometer test cell (4cm x 4cm x 1cm) after passing through a focusing lens. This lens is a fused silica lens having a diameter of one inch and a focal length of 15 cm.

The detection beam is provided by an Oriel Corporation model number 6697 3 mW Helium-Neon (HeNe) laser operating at a wavelength of 632.8 nm.

The probe beam first passes through an Oriel Corporation model 15220 spatial filter assembly. The diverging beam is collimated to a diameter of 1.5 cm. It then passes through a lens of focal length 35 cm. This produces a probe beam diameter of 18 μm at the focal point after being reflected ninety degrees by a small silvercoated back-surfaced mirror (1cm x 1cm) to the test cell. After passing through the test liquid the diverging probe beam is reflected ninety degrees by a 5.08 cm silvercoated mirror. Then it passes through a 5.08 cm crown glass lens which focuses the beam on a photodiode mounted on an x-z translator. This lens can be moved along the beam path to vary the intensity on the signal photodiode. The probe beam is positioned by moving the photodiode until the same change in output is observed for equal positive or negative angular displacements.

The probe beam responds to changes in the optical index of refraction associated with the generated acoustic wave. As the

density gradient traverses the probe laser beam, it causes the beam to deflect. This deflection is observed by monitoring the output of the photodiode.

The Antel Electronics, model number AR-S2 signal photodiode, manufactured by has a bandwidth from dc to 20 GHz. The photodiode output was amplified by a 100 kHz-1.3 GHz bandwidth model number 8447D Hewlett-Packard amplifier. The oscilloscope used was a Tektronics model 7854 with a 7B92A dual time base and a 7A26 dual-trace amplifier. The observed signal was digitized over a period of about five minutes at a repetition rate of 3 Hz. The captured waveform was then transferred to a DEC Minc-11/23 mini-computer interfaced to the oscilloscope. The stored data was then analyzed or transferred to a Masscomp 5500 for further analysis.

B. Calibration

1. Penetration Depth Determination for CS₂

The optical absorption coefficient α of pure CS₂ at 337 nm is large. To measure α , small amounts of CS₂ were added to propanol which absorbs UV radiation only weakly. The energy passing entirely through the test cell, measured by an energy meter is

$$E = E_0 \exp - [((1-f)\alpha_1 + f\alpha_2)x + a] \quad (3.1)$$

where

α_1 = absorption coefficient of pure propanol and the test cell,

α_2 = absorption coefficient of pure CS_2 ,

a = dimensionless absorption coefficient of the test cell,

f = volume fraction of CS_2 in propanol, and

x = length of test cell (4 cm).

In all cases of interest, f and a are very small so $\alpha_1(1-f)x+a \cong \alpha_1x$. The quantity α_1x can be measured by first measuring the energy, E_{max} , in the absence of the test cell and then the energy, E_0 , when the test cell full of propanol is placed in the beam path. We then have

$$E_0 = E_{\text{max}} \exp(-\alpha_1 x). \quad (3.2)$$

For our system, E_{max} was found to be 0.36 mJ and E_0 was found to be 0.34 mJ so $\alpha_1x=0.066$. We now can write Eq.(3.1) as

$$E = E_{\text{max}} \exp - [(0.066 + f\alpha_2)x]. \quad (3.3)$$

The total volume, V , of propanol for this experiment was 12 mL. Drops of CS_2 with a volume of 0.01 mL were added to the propanol so that

$$f = N(.01)/12 \quad (3.4)$$

where N is the number of drops. Energy transmission was measured after each drop. Using this technique α_2 was deduced to be $370 \pm 30 \text{ cm}^{-1}$ which implies a penetration depth for pure CS_2 of $27 \pm 2 \text{ }\mu\text{m}$.

2. Determination of the Excitation Beam Size

The size of a high energy laser beam at the focal point can be determined by various techniques. Knowing the diameter of the incoming collimated beam and the f-number of the focusing lens one can calculate the minimum spot size possible. This is useful only if the laser is operated in a single mode. The nitrogen laser beam was not very clean making focusing more difficult. As a result, other techniques were adopted to measure the beam size.

The spatial profile of the excitation beam at the focal point is an ellipse. The ratio of the two axes can be determined by exposing a photographic emulsion near the focal point. The size of the exposed portion of the film can then be measured under a microscope. The measured dimensions for the axes were found to be $150 \mu\text{m} \times 550 \mu\text{m}$. This probably does not represent the true dimensions of the beam due to overexposure of the film and difficulties in positioning the film at the focal plane. The technique does give a good indication of the ratio of the two axes which should remain constant.

The time duration of the acoustic response is primarily determined by the shorter dimension of the excitation pulse. By

comparing the experimental waveform to theoretical predictions one can determine the spatial width of the shorter dimension. When using this technique, the liquid must be carefully selected to obtain accurate results.

The alcohols used have fast relaxation times but small optical absorption coefficients at 337 nm. Dye must be added to get an observable signal. Although the dye increases the signal amplitude, it also increases the fluorescence output. Carbon Disulfide is strongly absorbing at 337 nm, but it is a slowly relaxing fluid. It has been shown by Thompson *et al.*²² that slow relaxation times can affect the shape and time duration of the acoustic wave generated. A desirable liquid would relax rapidly upon excitation and moderately absorb the UV laser pulse. A yellow or red alcohol-based fluid would seem to be ideal for this measurement. The liquid chosen for this measurement was a clean brand of scotch (Dewar's White Label). It has a fast relaxation time and presents little problem with fluorescence (at least in the visible spectrum). The shortest optoacoustic pulse was observed using this liquid. Comparison of the experimental waveform to theory is shown in Figure 3.2. The zero-crossing points are determined by the beam diameter. Using this technique we conclude that the dimensions of the excitation beam at the focal point are $90\mu\text{m} \times 330\mu\text{m}$.

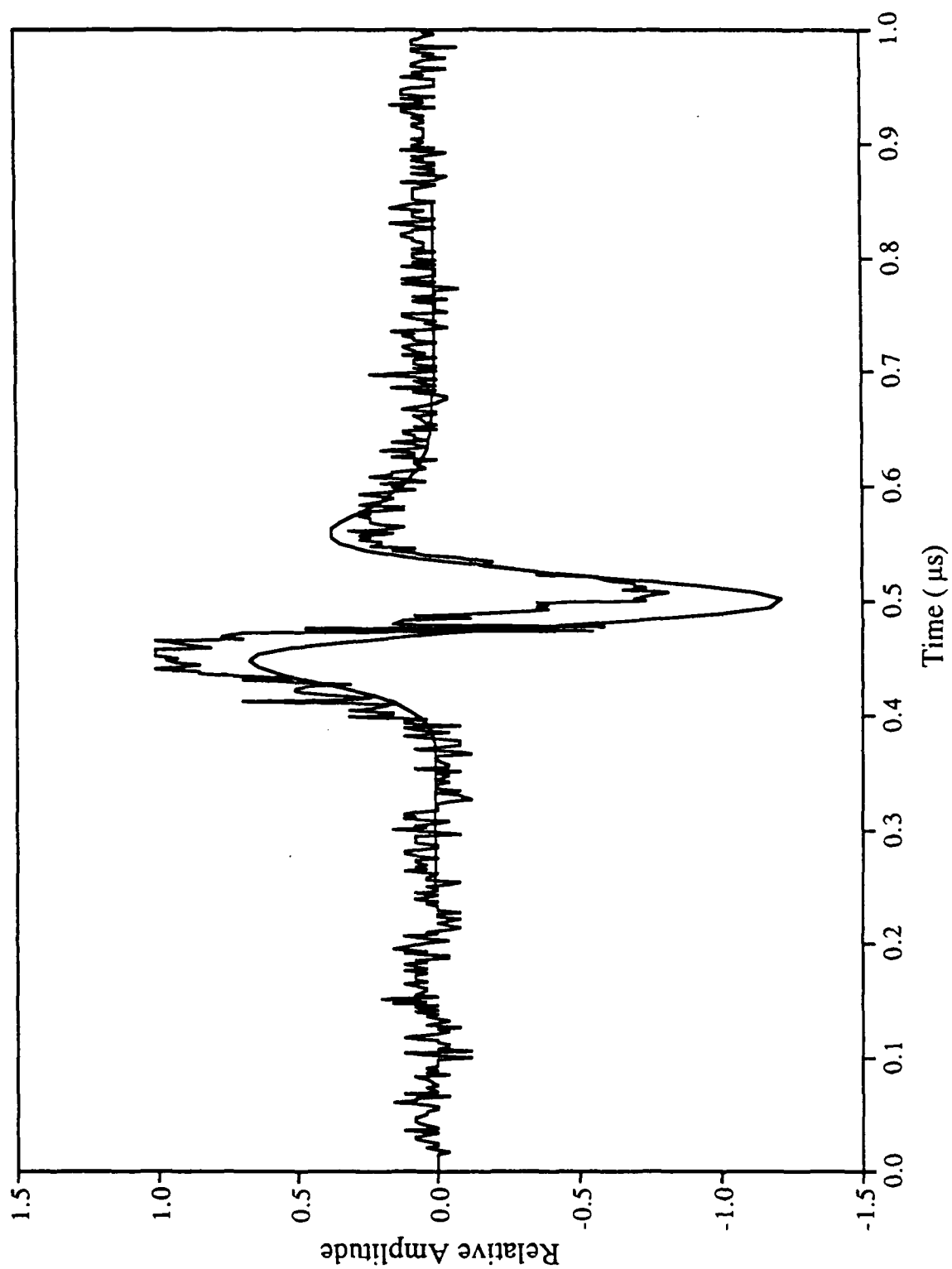


Figure 3.2

Chapter IV

Interpretation of Experimental Results

A. Linear Results

The first stage of this research was to determine how well existing linear macroscopic theories agree with the observed optoacoustic signal. Sullivan and Tam³⁹ explored the effect of beam diameters on the optoacoustic signal and found reasonable agreement with the theoretical description developed by Lai and Young.³⁷ The first set of measurements were designed to explore the effect of excitation energy, acoustic propagation distance, coefficient of thermal expansion, and optical absorption coefficient on the optoacoustic amplitude. The fluid used in these measurements was propanol doped with red dye. An expression for the amplitude A of the optoacoustic pulse is given by Eq. 2.15 as

$$A = (\alpha\beta E / 8\sqrt{\pi}c_p)(c/r)^{1/2}\tau_e^{-3/2} \quad (4.1)$$

where

- α = optical absorption coefficient,
- β = coefficient of thermal expansion,
- E = laser pulse energy,
- c_p = specific heat at constant pressure,
- c = acoustic velocity,
- r = propagation distance,
- $\tau_e = (\tau_p^2 + \tau_a^2)^{1/2}$,
- τ_p = laser pulse duration, and
- τ_a = acoustic transit time.

The laser pulse energy was varied by placing thin glass microslides (0.23 mm thick) in the beam path. The slides were calibrated with a Molectron J3-09 Joule meter using a JD 1000 Joule meter display. The precision of the energy is $\pm 2 \mu\text{J}$. The measured energy delivered to the test cell as a function of the number of glass slides is shown in Fig. 4.1. Figure 4.2 is a plot of optoacoustic signal amplitude vs laser pulse energy. The linear relationship between A and E is in agreement with equation 1. This is expected as long as

$$\Delta T + T_o < T_b \quad (4.2)$$

where

$\Delta T = \Delta E / c_p$, T_o = initial temperature, and T_b is the boiling temperature of the liquid.

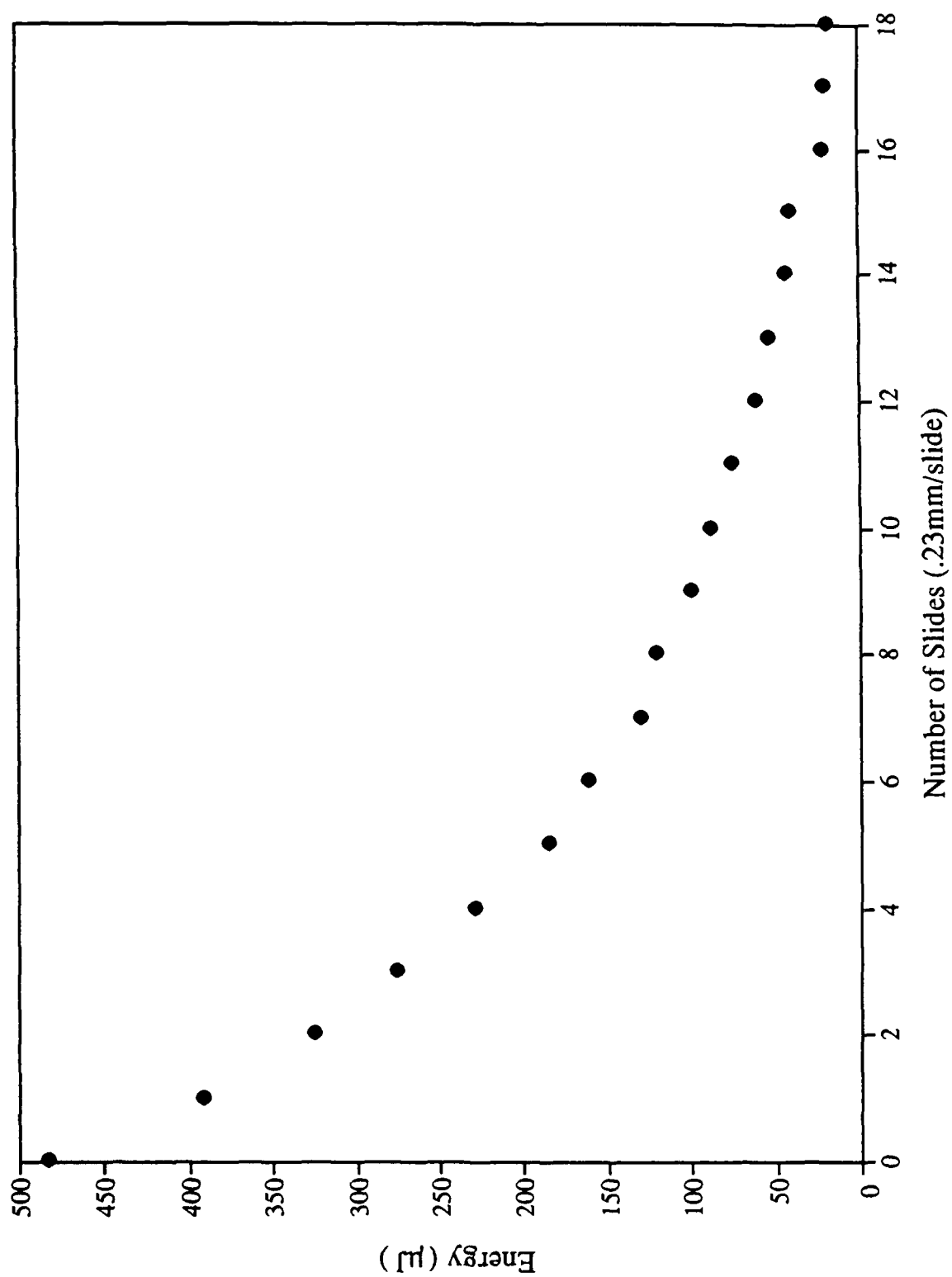


Figure 4.1

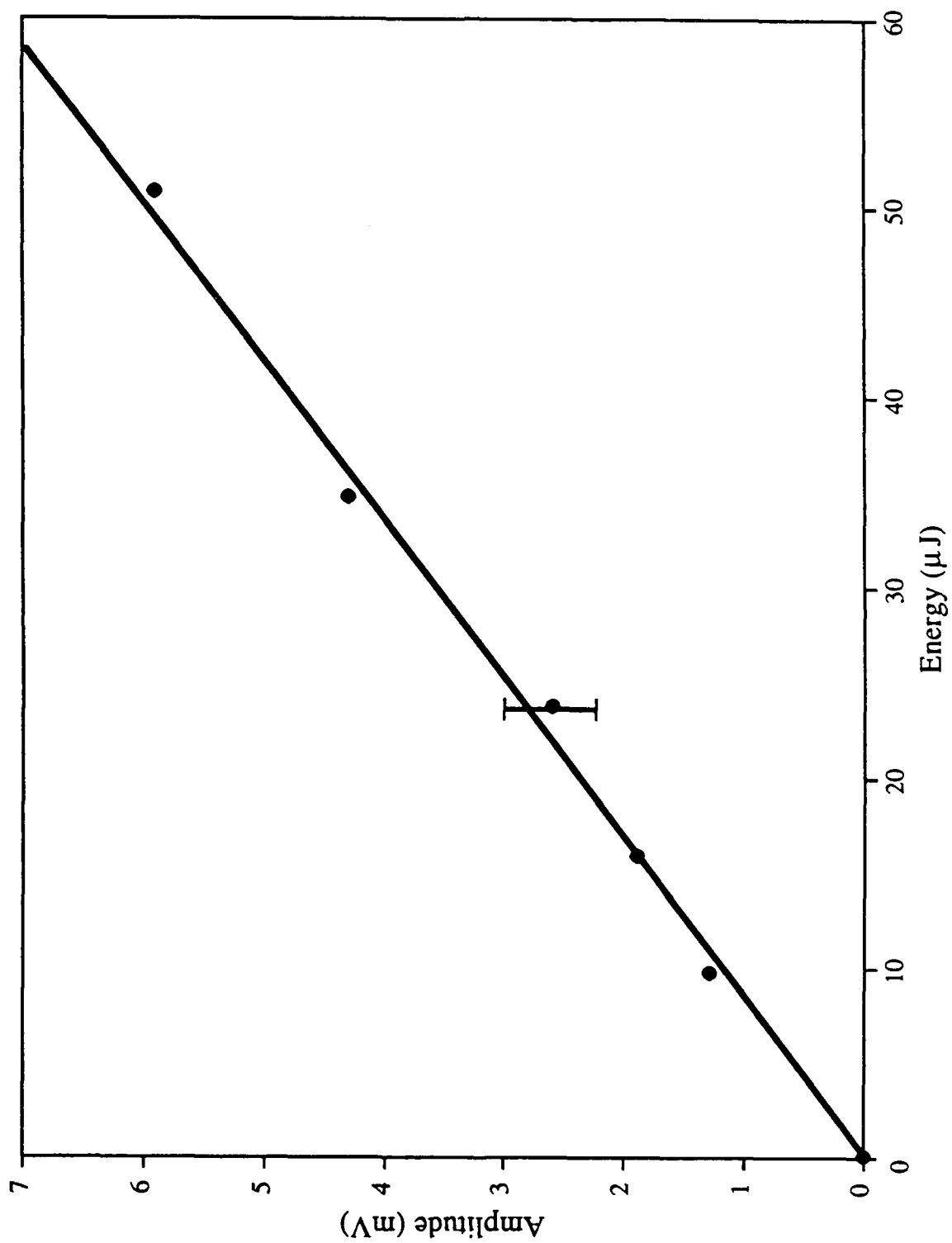


Figure 4.2

The error bar represents one standard deviation in the slope from the theoretical line. The theoretical line was found using a least squares fit of the experimental data. The standard deviation σ is given from Ref. 40 as

$$\sigma = \sqrt{\frac{1}{N-1} \sum \left(\frac{A_{\text{exp}} - A_{\text{Theory}}}{E - E_0} \right)^2} \quad (4.2)$$

where

- A_{exp} = Amplitude of experimental data,
- A_{Theory} = Amplitude of theory,
- E = Energy of laser pulse,
- E_0 = 0, and
- N = Number of data points.

The next parameter considered was the propagation distance r . Increasing the propagation distance of the acoustic wave was achieved by moving the excitation beam away from the probe beam. This was done by placing mirror M1 (see Figure 3.1) in an optical mount and making rotational movements about the horizontal axis. The propagation time could be determined by monitoring the optoacoustic pulse on the oscilloscope. Knowing the sound velocity and the propagation time, the propagation distance was calculated.

The distance between M1 and the test cell should be large enough so the excitation beam remains perpendicular to the test cell while increasing the acoustic propagation distance. This distance was

about 1 meter. The maximum separation distance between the two beams was only 1.5 mm. This gives a maximum angle of deviation of .086 degrees.

The results of this measurement are shown in Figure 4.3. The reference propagation distance and amplitude are 1 mm and 1 mV, respectively. This graph shows that the decrease in signal amplitude is proportional to $1/\sqrt{r}$ which is characteristic of cylindrical spreading. The error bar represents one standard deviation from the theoretical line. This discrepancy is acceptable and the experimental results are considered to be in agreement with Eq. 4.1.

According to Equation 4.1, the optoacoustic amplitude should be directly proportional to the coefficient of thermal expansion. To test this dependence, liquids with different values of β were used. The input energy density was made constant by adding red dye to make the optical absorption coefficient of each test liquid the same. The results of these measurements are shown in Figure 4.4. The error bar represents typical uncertainties in the amplitude measured for propanol as determined in previous measurements. The linear relationship is in agreement with Equation 4.1.

Another point of comparison is variation of signal strength with the optical absorption coefficient α . According to Equation 4.1, the acoustic amplitude should vary linearly with α . This measurement involved adding red dye to the test liquid to increase α . The results of this measurement are plotted in Figure 4.5. The simple description of the beam used to derive Eq. 4.1 is insufficient for large absorption.

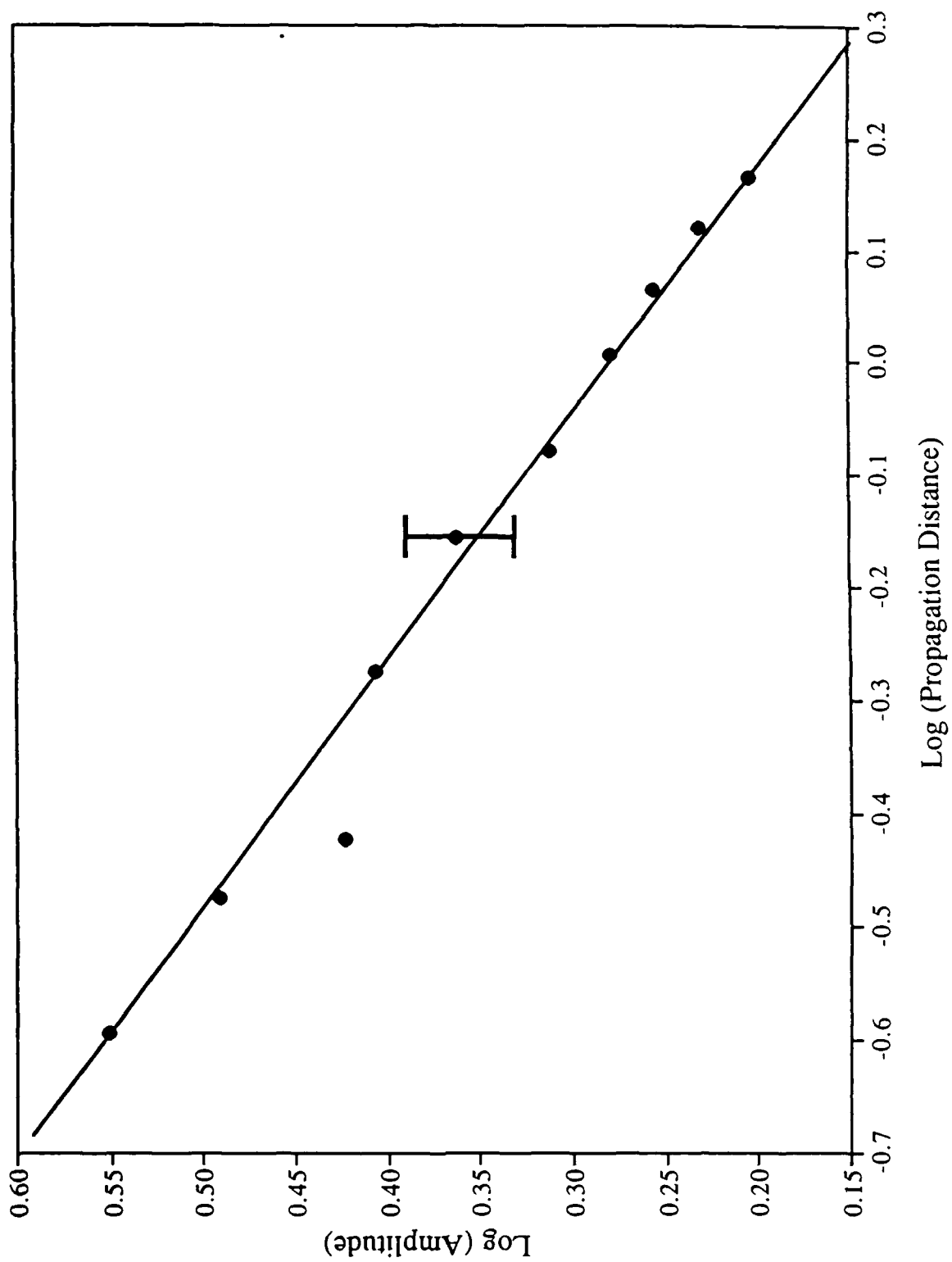


Figure 4.3

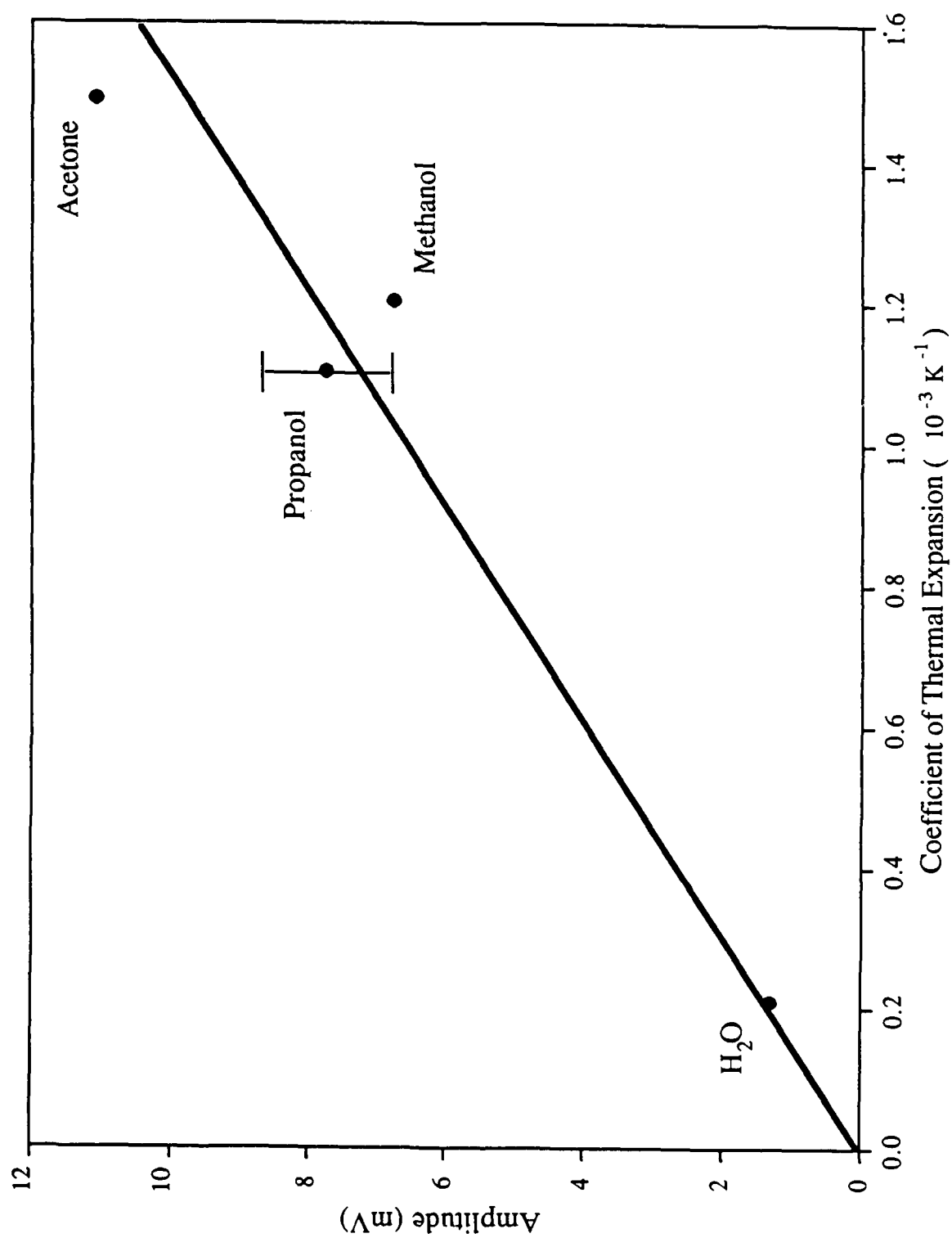


Figure 4.4

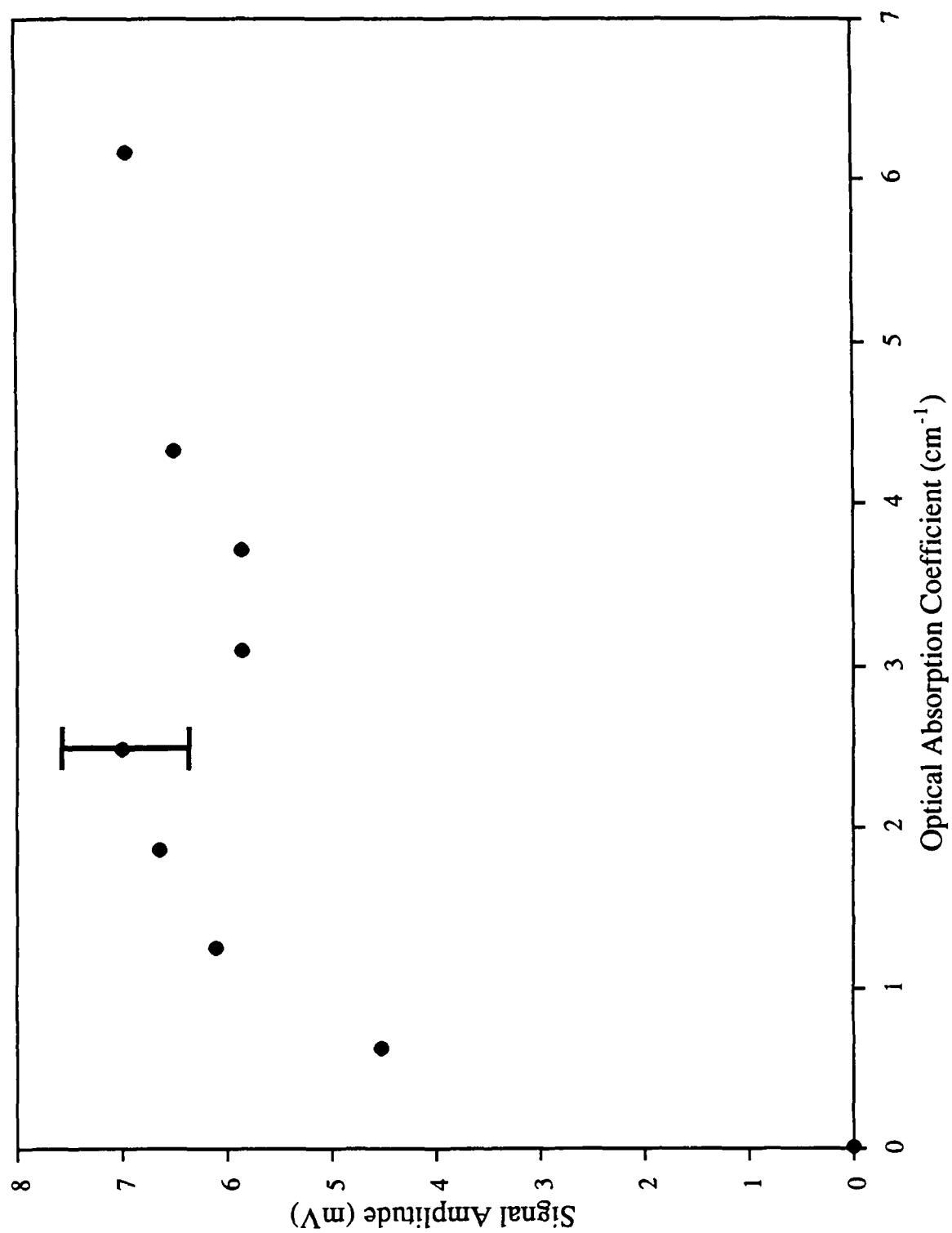


Figure 4.5

As the probe beam propagates alongside the excitation beam, it undergoes a deflection which is a result of the sum of all the gradients in refractive index encountered in the fluid. The probe beam will be most sensitive to the index gradients near its focal plane if the gradients near its focal plane are confined to spatial dimensions on the order of the probe beam diameter. However, there will be some deflection due to density gradients all along the probe beam path. When the absorption coefficient is small (penetration depth large), much of the excitation beam passes entirely through the test cell. In this case, an increase in absorption coefficient does, indeed, give rise to an increased optoacoustic signal. Once the absorption coefficient is large enough to trap all the excitation energy within the test cell, further increases in the absorption coefficient have a much smaller effect. This is because the total optical energy within the test cell is now constant. As a result, the amplitude of the observed optoacoustic signal will remain constant. Again, the error bar represents typical uncertainties in previous propanol measurements.

Another quantity of interest is the absolute magnitude of the optoacoustic signal. This was measured with a calibrated Mediateknisk Institut PVDF hydrophone. The active element of the hydrophone was 1 mm. The results of this measurement are shown in Figure 4.6 along with predictions from Eq. 2.12. The measured pressure wave agrees reasonably well with theory considering the limited time response of the hydrophone.

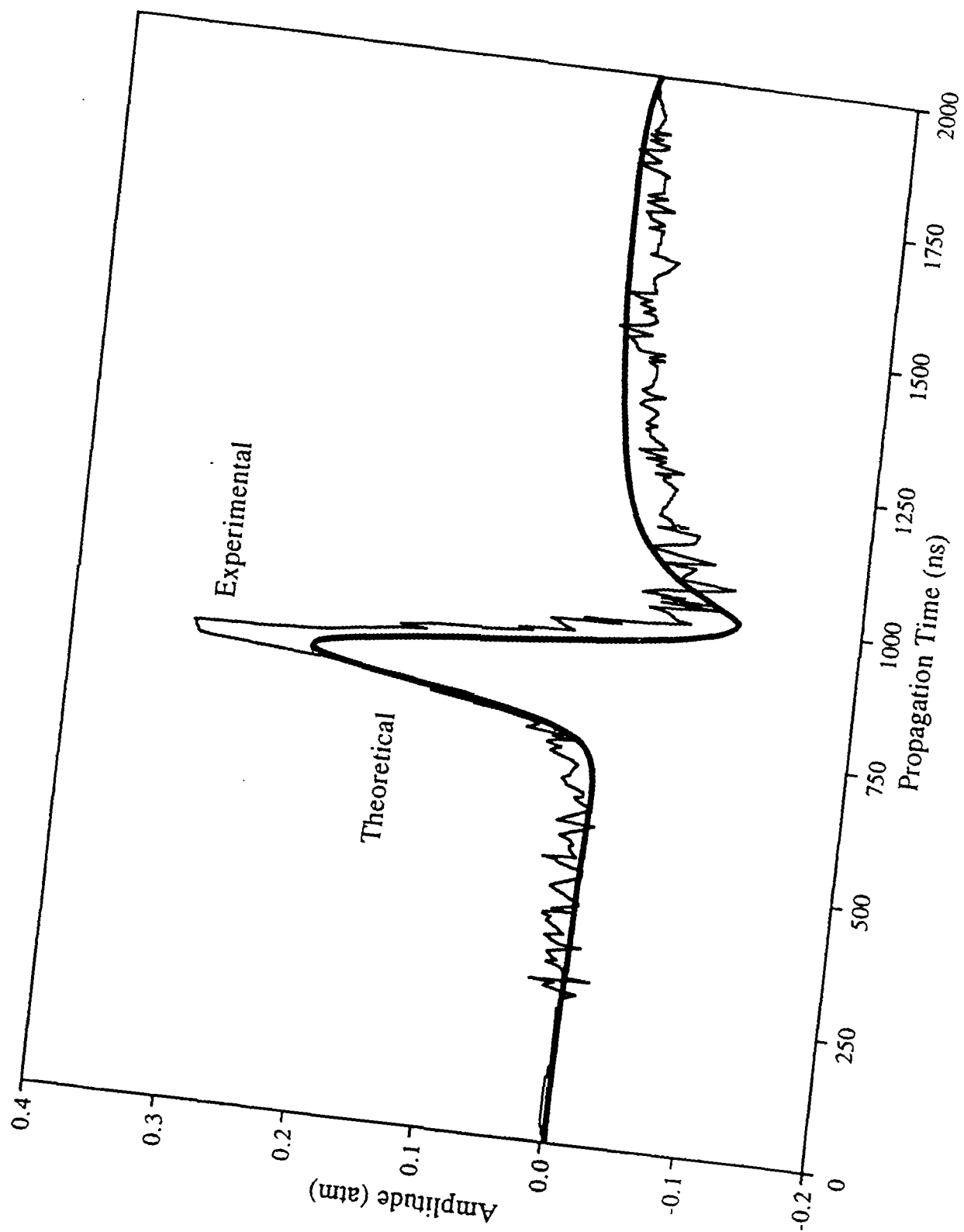


Figure 4.6

B. Nonlinear Results

One objective of this investigation was to examine nonlinear phenomena. The liquid chosen for this part of the study was carbon disulfide. It absorbs ultraviolet radiation quite strongly giving rise to high energy densities. We wanted to see how the peak amplitude of the optoacoustic response varied with laser pulse energy at intermediate and high energy densities. The results of these measurements are shown in Fig. 4.7. This graph can be separated into three regions.

Region 1: $0 \leq E < 18 \mu\text{J}$,

Region 2: $18 \mu\text{J} \leq E \leq 80 \mu\text{J}$, and

Region 3: $80 \mu\text{J} < E \leq 298 \mu\text{J}$.

In region 1, the optoacoustic amplitude varies linearly with input energy. A transition occurs at $E=18 \mu\text{J}$ designating the beginning of region 2. In region 2, the amplitude appears to again vary linearly but with a larger slope than in region 1. A second transition occurs at $E=80 \mu\text{J}$. In region 3, the optoacoustic amplitude varies nonlinearly with input laser pulse energy.

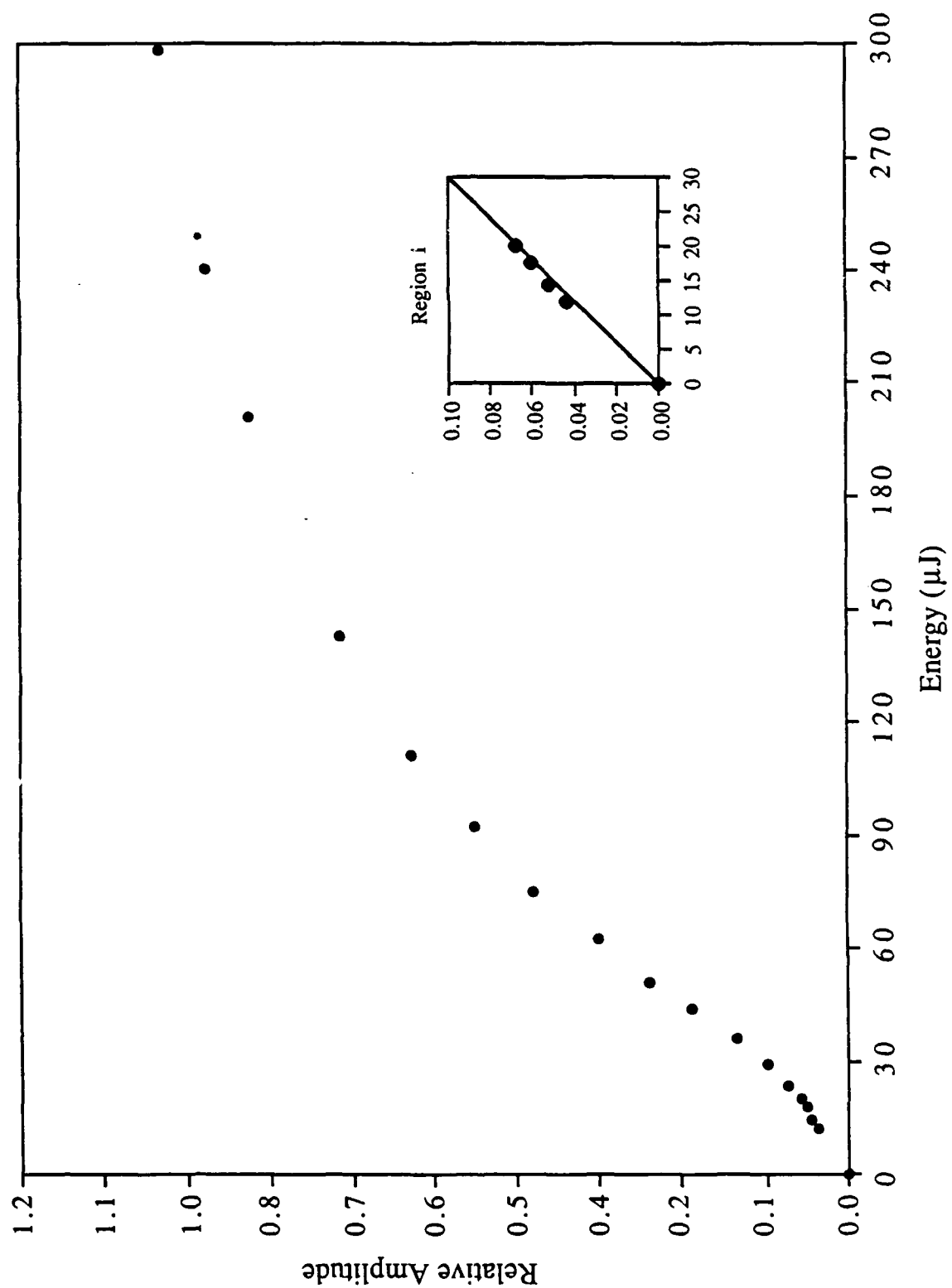


Figure 4.7

A few experimental observations should be noted. At $E=50\text{ }\mu\text{J}$ vapor bubbles began to appear. As the excitation energy was increased vaporization became more apparent. From the specific heat⁴¹ and mass of the excitation volume of liquid, the boiling temperature of CS_2 (319 K)⁴² should be reached with a laser energy of $18\text{ }\mu\text{J}$. This energy appears to coincide with the end of the first region. From this observation, we conclude that the thermal expansion mechanism is dominant in region 1. Since there is an increase in slope in region 2, a different and more efficient conversion mechanism must be present. Vaporization is the obvious candidate. Microscopically, this process can be viewed as a cluster absorbing a second photon before it has a chance to relax or be reunited with the molecules dissociated due to the first photon. In region 3, the input energy is well above the vaporization threshold suggesting that this portion of the curve may be dominated by gas phase properties. Comparing region 2 to region 3 it can be seen that the optoacoustic conversion efficiency decreases with further increase in laser pulse energy. This suggests there is a region of optimum conversion efficiency. Referring to Eq. 2.29, the optoacoustic amplitude is proportional to the coefficient of thermal expansion β . The American Institute of Physics handbook⁴³ gives β as a function of temperature for liquid CS_2 as

$$\beta = a + 2bT + 3cT^2 \quad (4.3)$$

where

$$\begin{aligned} a &= 1.1398 \times 10^{-3} \text{ C}^{-1}, \\ b &= 1.37065 \times 10^{-6} \text{ C}^{-2}, \text{ and} \\ c &= 1.91225 \times 10^{-8} \text{ C}^{-3}. \end{aligned}$$

For an ideal gas,

$$\beta = \frac{1}{T}. \quad (4.4)$$

The expansion coefficient for the three regions are then written as

$$\beta_1 = a + 2bT + 3cT^2, \quad (4.5)$$

$$\beta_2 = (1-f)\beta_1 + f\beta_3, \text{ and} \quad (4.6)$$

$$\beta_3 = \frac{1}{T} \quad (4.7)$$

where f is some weighted fraction of the excitation volume which has been converted to gas. It is assumed that the fraction $f=0$ for $E=18 \mu\text{J}$ and increases linearly until $f=1$ for $E=80 \mu\text{J}$. The change in temperature is related to the laser pulse energy by the heat capacity of the liquid

$$\Delta T = \frac{\Delta E}{C_p}. \quad (4.8)$$

With the use of Eq. 4.8 and Eq. 4.1, the effects of a changing thermal expansion coefficient can be plotted as a function of laser pulse energy. This is shown in Fig. 4.8. Note that the temperature dependence of β successfully explains the amplitude variation as a function of E for all but the latter part of region 3. This discrepancy will be discussed later.

The agreement between data and theory gives rise to some physically appealing results. In region 1 the fluid is composed mainly of clusters of molecules. In region 3, the curve can be explained in terms of an ideal gas suggesting that most of the clusters are broken apart. Region 2 then, must represent a transition regime of vaporization. Recall that for $E = 50 \mu\text{J}$, vapor bubbles began to form. This corresponds to a value of $f=0.5$. This suggests that when 50% of the molecules have been dissociated from their clusters, vapor bubbles began to form.

In previous calculations we have assumed that the absorption coefficient determines the length of the excitation region. The decreased efficiency compared to prediction displayed in Fig. 4.8 suggest that the size of the excitation region may be increased at high energies. In this case the original excitation region is completely vaporized and cannot absorb further laser energy. As a result, a portion of the laser energy will penetrate deeper into the liquid.

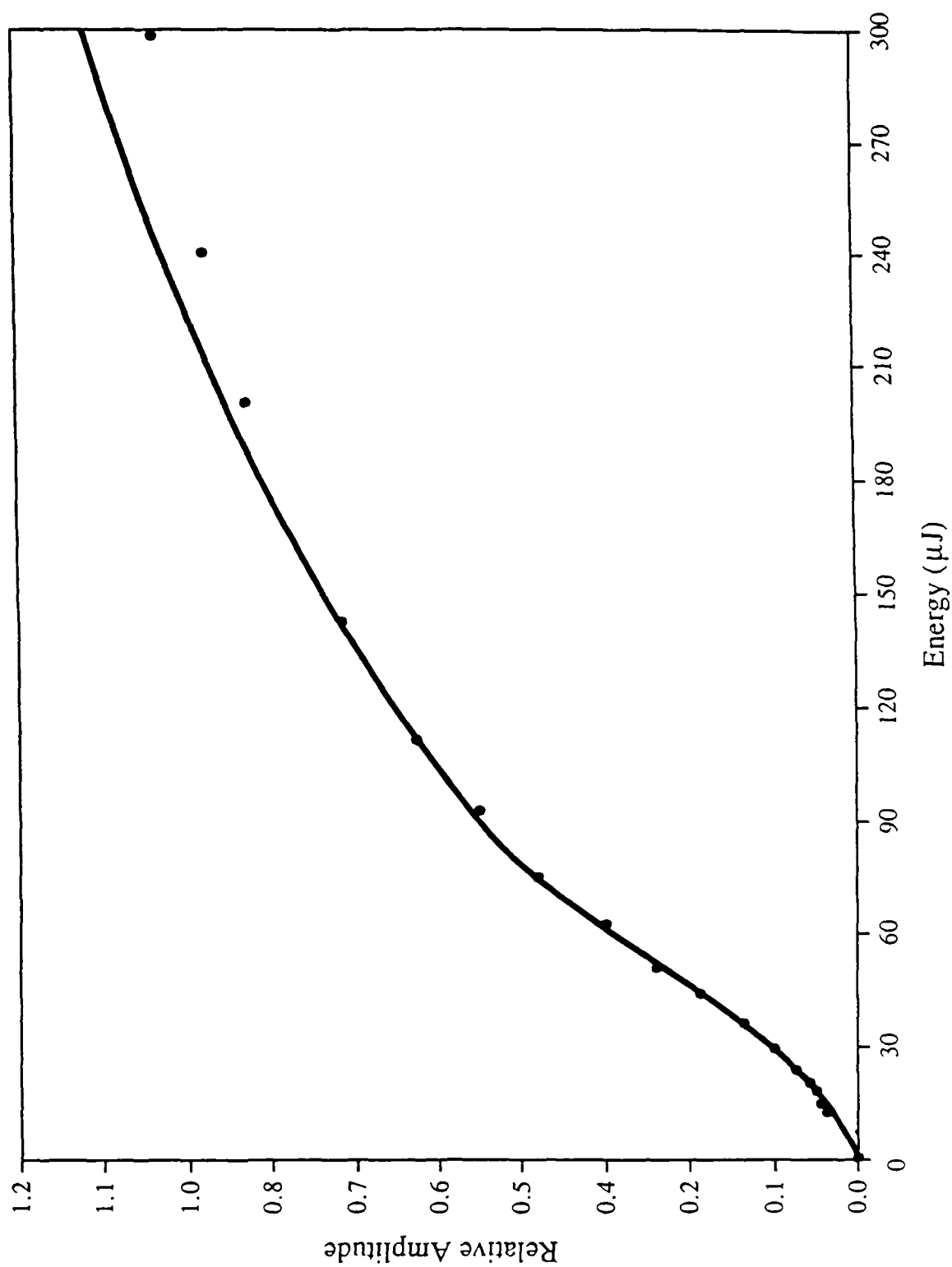


Figure 4.8

The latent heat of vaporization is the energy required to completely vaporize a particular volume of liquid. This corresponded to a laser pulse energy of 278 μJ in this experiment.⁴⁴ In this experiment, we achieved a maximum energy of 298 μJ . We propose that the first 278 μJ of energy vaporizes the original excitation volume and any excess energy penetrates deeper in the fluid.

We want to calculate the number of CS_2 molecules it takes to absorb the 20 μJ of energy above the latent heat of vaporization. Dividing the total number of molecules in the excitation volume by the latent heat of vaporization gives

$$\frac{6.02 \times 10^{15} \text{ molecules}}{278 \mu\text{J}} = 2.16 \times 10^{13} \frac{\text{molecules}}{\mu\text{J}} \quad (4.9)$$

This represents the number of CS_2 molecules it takes to absorb 1 μJ of the laser pulse. Multiplying Eq. 4.9 by 20 μJ results in

$$(2.16 \times 10^{13} \frac{\text{molecules}}{\mu\text{J}})(20 \mu\text{J}) = 4.32 \times 10^{14} \text{ molecules.} \quad (4.10)$$

This is the number of molecules needed to absorb the additional 20 μJ of laser energy. The number of moles is

$$\frac{4.32 \times 10^{14} \text{ molecules}}{6.022 \times 10^{23} \frac{\text{molecules}}{\text{mole}}} = 7.17 \times 10^{-10} \text{ mole.} \quad (4.11)$$

Multiplying by the molecular volume yields

$$(7.17 \times 10^{-10} \text{ mole})(60.4 \frac{\text{cm}^3}{\text{mole}}) = 4.33 \times 10^{-8} \text{cm}^3. \quad (4.12)$$

This is volume of liquid CS_2 which absorbs the energy above the latent heat. The spatial profile of the excitation beam at the focal point was found to be an ellipse. The length of the major and minor axes were found to be $330 \mu\text{m}$ and $90 \mu\text{m}$, respectively. Dividing Eq. 4.12 by the cross-sectional area of the beam gives

$$\frac{(4.33 \times 10^{-8} \text{cm}^3)}{\pi(165 \times 10^{-4} \text{cm})(45 \times 10^{-4} \text{cm})} = 1.8 \times 10^{-4} \text{cm}.$$

The $1.8 \mu\text{m}$ is the depth of additional penetration in the fluid. The results of including this added penetration depth in the optoacoustic amplitude calculation can be seen in Fig. 4.9.

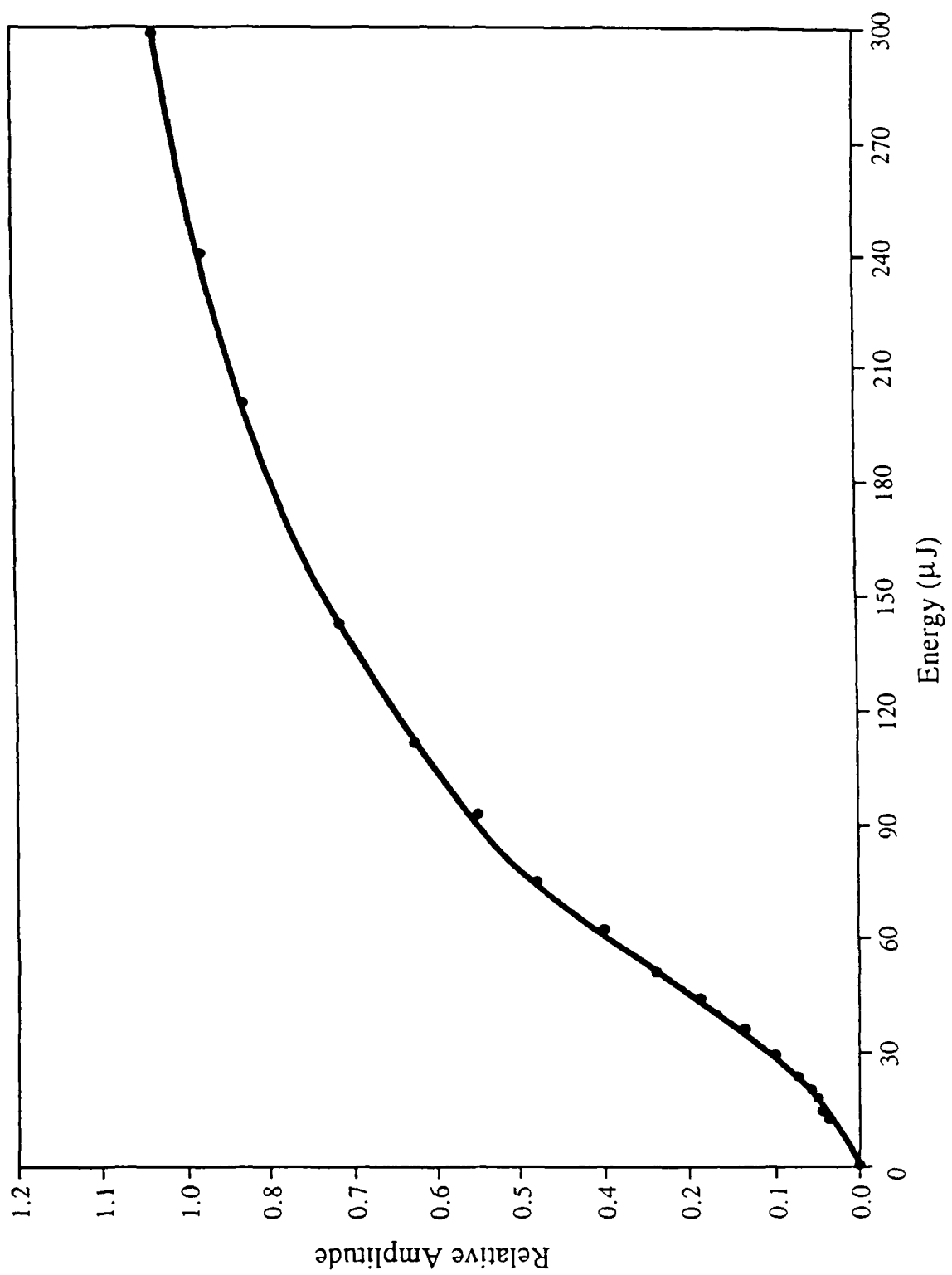


Figure 4.9

Chapter V

Conclusions and Suggestions for Future Work

The optoacoustic effect has been studied theoretically and experimentally. Microscopic and macroscopic descriptions have been considered. We have shown that the existing macroscopic theory developed by Lai and Young³⁷ predicts the observed linear behavior.

Nonlinear effects have been observed experimentally. This behavior has been explained in terms of dynamically changing temperature dependent coefficients of thermal expansion and attenuation. A rapid change in the acoustic amplitude occurs at the boiling temperature. The high temperature regime (region 3) behaves as an ideal gas. The low temperature regime (region 1) behaves as an ideal liquid. Vapor bubbles appear when the ratio of an ideal liquid to an ideal gas in the fluid mixture is one to one. These observations are consistent with the cluster model description of the molecular structure of the liquid. As the number of photons are increased more molecules are stripped from their clusters. Region 2 probably begins when additional molecules are excited before the first molecules or groups of molecules recombine with their cluster or a neighboring one. Also, the optoacoustic conversion

efficiency is at a maximum in region 2 and decreases in region 3. From this, we can conclude that vaporization does increase the optoacoustic conversion efficiency as previous authors have suggested but only when a fraction of the fluid mixture is still acting as an ideal liquid. Once the mixture is dominated by the gas, the conversion efficiency will decrease.

Several suggestions for future work consisting of different techniques and different instrumentation should be considered. Increased time resolution and optical energy density would provide additional information. Specifically, improved resolution will allow studies of molecular relaxation and/or recombination processes in liquids other than CS_2 . Increasing the energy per unit time will increase the number of photons per cluster, thus, increasing the probability of a cluster dissociation. This can be achieved by choosing a liquid that absorbs a particular optical wavelength quite strongly, shortening the time duration of the laser pulse, focusing the beam more tightly, or all of the mentioned. In addition, a higher speed instrument should be used for data acquisition. Thinner microslides (laser energy attenuators) should be used to decrease the size of the incremental change in laser pulse energy. By increasing the number of data points, small effects may be revealed not observed in measurements reported here.

Measurements should be repeated in other liquids to determine the dependence of laser pulse energy on the optoacoustic amplitude near the boiling point, latent heat of vaporization, and at

energies greater than the latent heat. With sufficient data, one may be able to reveal structural properties of liquids on a molecular level.

Measurements should also be made in liquid mixtures. In general, adding small quantities of a fast relaxing liquid to a slow relaxing liquid shortens the relaxation time of the mixture. Monitoring the changing relaxation time as a function of the mole fraction of the fast relaxing liquid may provide information of how the absorbed energy is redistributed or dissipated through the energy levels of the molecules.⁴⁶

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[REDACTED]

he attended Hendrix College in Conway, Arkansas where he received a Bachelor of Arts Degree in physics in 1984. Mr. Cheyne then attended the University of Mississippi in Oxford, Mississippi where he received a Master of Arts Degree in Physics in 1986. He continued his education at the University of Mississippi to work on a Doctor of Philosophy Degree in physics.

Mr. Cheyne has spent some of his time at the University of Mississippi teaching introductory Astronomy and teaching night observation sessions to many local and nonlocal organizations. Mr. Cheyne is a member of the Acoustical Society of America. His career objectives are to teach physics at the undergraduate level and perform basic research in physics at a university.
[REDACTED]
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A few of Mr. Cheyne's interests consist of running and participating in most other sporting events.

His main concern is trying to maintain a straight walk toward the Lord Jesus Christ. He is also dedicated to serve God in whatever way God's will desires.